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Optimisation of thermoelectric green tape characteristics made by the tape casting method

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Abstract

The variables of the tape casting process were optimised to produce green tapes made out of thermoelectric material powders, with sufficient strength to be handled during the post-processing stage. Most of the mechanisms and analysis concerning the organic additions to the powder, to create a flexible green tape, have been explored. The types of organic additives used in the formulation of the slurry, the effect of the ratio of the organic additives on the final physical characteristics of the green tapes are given. The manufacture of tapes characterised by the powder size, slurry viscosity, apparent and bulk densities, tensile strength, and adhesion properties is outlined. All these parameters were optimised for the specific task of fabricating a thermoelectric generator, as a monolithic block, made out of multi-layers of different materials. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Semiconducting; Polymer; Thermoelectric effect; Powder metallurgy

1. Introduction

Tape casting is a low-cost process for making high-quality laminated materials, for which good thickness control and surface finish are required. The process is important for making large-area, thin, flat ceramic parts. A 'Tape' is formed by the use of a scraping blade or 'doctor blade', which evenly coats a moving surface with slurry. The coating dries to from a green tape which can be cut into different shapes. The cut tape is fired to form a plane flat solid ceramic shape.

The main applications for tape casting is in the production of capacitors and multi-layer printed circuit boards (PCB). It is now possible for example to print and fire as many as 80 alternating layers of conductors and insulators.

Green tapes permit the creation of complex high-density circuits with more input/outputs and functions per cubic inch than previously available [1]. Other applications where tape casting is used extensively are Solid Oxide Fuel Cell (SOFC) fabrication, Piezoelectric ceramic for transducers and Silicon carbide (SiC) for heat exchanger [2–5].

In this paper, the tape casting method has been applied as a production method for the thermoelectric generators. The introduction of tape casting process to the fabrication of thermoelectric generators, represents a departure from their traditional methods of fabrication, which are complex and result in the very high cost of generators.

The role played by the organic additives, in the tape casting process is of a prime importance. They effect the strength, flexibility, arrangement and distribution of the powder particles throughout the green tape. The properties of the green tape are reflected in the quality of the final product of the sintered tape. Hence, it is very important to evaluate the characteristics of the green tape in term of the variation in the organic additives and the process variables of creating the tape.

2. Experimental procedure

2.1. Starting thermoelectric powder materials and organic additives

Iron disilicide ($FeSi_2$) and Silicon germanium (SiGe) alloy powders were both Synthesised by the mechanical alloying technique [6].

Two organic formulation systems were used in this project, the first was with Poly-vinyl-butyral (PVB) and the second was with Poly-methyl-methacrylate (PMMA) bin-

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Table 1
Types of PVB organic additives used in the slurry composition for the thermoelectric green tapes

Function	Material
Thermoelectric powder	SiGe or $FeSi_2$
Dispersant	Glycerol trioleate
Solvent 1	Trichloroethylene
Solvent 2	Ethanol
Plasticizer	PEG600/PEG1000
Plasticizer	Diethyl phthalate
Plasticizer	Dibutyl phthalate
Binder	Mowtial B20H (PVB)
Binder	Mowtial B70H (PVB)

Table 2
Types of PMMA organic additives used in the slurry composition for the thermoelectric green tapes

Function	Material
Thermoelectric powder	$FeSi_2$
Dispersant	Glycerol trioleate
Solvent 1	Trichloroethylene
Solvent 2	Ethanol
Plasticizer	Dibutyl phthalate
Binder	Acryloid B67 OR B-7MEK

der. Tables 1 and 2 show the general slurry composition with PVB and PMMA binders.

The PVB binders were obtained from Hoechst representative in the UK (Crestchem Ltd.), under the commercial name of Mowtial Resins and were supplied as a free-flowing fine-grained powder. The Mowtial has grades of 20, 30, 40, 60 and 70. The number refers to the increasing degree of polymerisation. A combination of two grades of Mowtial B20H and B70H were used according to the advice of the manufacturer. The plasticizer Polyethylene Glycol (PEG) was obtained again from Hoechst, in two different molecular weights grades, of 600 and 1000 and both are obtainable in a liquid/solid form. The rest of the plasticizers, Diethyl phthalate and Dibutyl phthalate, both in a liquid form, were obtained from BASF UK, under the commercial name of 'Palational A' and 'Palational C', respectively. The solvents were both 99.9% pure and obtained from Fison UK. The PMMA binders were of two types and obtained from Rohm and Hass (USA). The first under the commercial name of Acryloid B-67 was in the form of transparent white grains. While a second had the commercial name of Acryloid B-7 MEK, and was in the form of viscous liquid, with the binder already dissolved into a Methyl-ethyle-ketone solvent (MEK).

The PVB binder system was selected in this project because of its excellent green tape characteristics, the main reason why it is the most commonly used binder for the tape casting processes in the ceramic industry. The PMMA binder was used due to its low burnout temperature and its low char content during the pyrolysis process, when compared to the PVB binder system formulation [7,8].

2.2. Preparation and mixing of thermoelectric slurry

Mixing and homogenisation of the slurry was carried out in a closed polythene jar, with a flat 'T' shape blade. The blade was rotated by a 12 V electric motor, capable of a maximum rotational speed of 60 rpm. The speed of the motor was varied by altering the supply voltage. The slow rotation of the blade and its shape minimised the creation of air bubbles within the slurry.

Before the mixing starts, a mixture of solvent, thermoelectric powder and dispersant was sonicated first for 10 min using an ultrasonic probe. The addition of PVB binders to the mixture, was usually done 5 h after the mixing started. The plasticizers were added after 20 h, and the whole mixture was left to homogenise for an additional 8 h. In the case of the PMMA binder, the binder was added immediately after sonification, since this particular binder possessed very strong dispersing power for the powder within the mixture. The plasticizer was then added after 1 h and the mixture was left to homogenise for an additional 20 h.

2.3. Tape casting of the green tapes

After the mixing and the homogenisation of the slurry was completed, the slurry was de-aired. This process, was carried in a polythene jar containing slurry. The jar was evacuated using a vacuum pump set to a pressure of 200 mbar absolute.

After the de-airing process, the slurry was cast on a casting surface or substrate. This was either glass, polythene or PTFE.

The casting table itself has two steel shafts driven by stepper motors. The shafts move a steel rod in the x and y directions. The steel rod in turn, draws an assembly comprising the slurry reservoir, and two doctor blades to control the slurry thickness. Casting speeds were varied by a stepper motor control drive board, up to a maximum casting speed of 40 cm min^{-1}.

The casting unit has two casting blades, to control the slurry flow onto the casting surface or substrate. The casting blades can be adjusted vertically with a pair of screws on the sides of each blade. Fig. 1, shows schematically the arrangement of the casting unit.

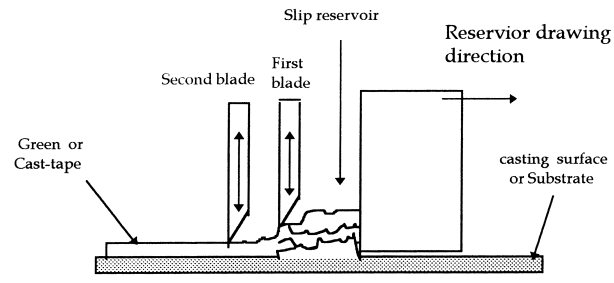

Fig. 1. Schematic of two blades casting unit.

2.4. Characterisation

The thermoelectric powder particle size was characterised using a laser particle size analyser (Malvern Instrument Plc). Powder agglomeration before after sonification was characterised using a laser particle size analyser, electron microscope and an optical microscope connected to a computer screen through a video camera, where the powder particle size measurements were carried out through an image analysis software 'Lucia' from Nikon Ltd.

The viscosity measurements for the slurry were conducted with Brookfield Digital Viscometer LV series model LVDV-I+ made by Brookfield Engineering Lab. Inc. The measurement were carried out using a small sample adapter of 8–10 ml.

Characterisation of the quality of the cast tapes has been carried out in term of surface texture, cracks, tensile strength, adhesion to substrate and the bulk and apparent densities. These qualities vary with the amount of inorganic to organic additives in each tape and to the relative quantities of binder and plasticizer.

In order to assess these variations and their effect on tape quality objectively, two parameters have been introduced, the ratio of the inorganic to the total present in tape given the symbol x, and the ratio of binder to plasticizer given the symbol y.

Where

$$x = \frac{\text{Inorganic}}{\text{Inorganic} + \text{Organic}} \times 100$$

and

$$y = \frac{\text{Binder}}{\text{Plasticizer}}$$

Beside these two, other parameter effects such as the ratio of the solvent components within the mixture, or the thickness of the tapes can be easily incorporated along with the effects of the x and y parameters to assess the quality of the tapes.

The measurement of the tensile strength of the cast tape was carried out on specimens, cut from each tape. The test specimen was 60 mm long, with a neck of 30 mm in length and 10 mm in width. These specimens were hung on a spring balance, and weights were added gradually until the tape fractured.

The measurement for the bulk and the apparent densities is carried out as follow [9].

1. The dry green tape is weighed accurately in air, and recorded as W_1.
2. The green tape is then soaked in water for 72 h, in order to allow a sufficient time for the water to fill the pores of the tape. The tape is weighed immersed in water, and the weight is recorded as W_2.
3. The sample is taken out of the water, and the moisture of the surface is removed with lightly dabbing the surface with a damp cloth, and the tape is then weighed in air as W_3.

The apparent density of the tape is then calculated from

$$\rho_{\text{app}} = \frac{W_1 \rho_{\text{w}}}{W_1 - W_2}$$

The bulk density of the tape is then calculated from

$$\rho_{\text{bulk}} = \frac{W_1 \rho_{\text{w}}}{W_3 - W_2}$$

Where ρ_{w} is the density of the water at the temperature of weighing.

The accuracy of this method was tested against the accuracy of the Auto-pycnometer, giving an error of 4–5%, when compared with the Pycnometer results.

3. Results and discussion

3.1. Thermoelectric powder characterisation

Well characterised powders were necessary to fabricate a device with high reliability and reproducibility. The most important characteristics of a powder were identified as particle size distribution, the surface area and agglomerate size within the powder.

The thermoelectric powders in this project were produced by the mechanical alloying method. Such powder particles have no regular shape, and have a narrow range of particle size distribution. The narrow range of particle size distribution has an advantage over the mono-size powder particles, since it is an effective way of increasing the packing factor. This is due to smaller particles filling spaces among the larger particles, thus reducing the influence of the surface particle roughness during the powder packing.

The second aspect which should be considered when optimising the tape quality is the surface area of the powder, which is inversely proportional to the average particle size. The surface area of the powder influences the microstructure of the green tape and the fired tape in an opposite way. It is true that increasing the surface area of the powder by decreasing its average particle size, is desirable from the sintering point of view. But on the other hand, since the mechanism of the organic reaction is based on surface chemistry, increasing the surface area of the powder, involves the use of a larger amount of organic additives to cover this increase. This represented a problem for the pyrolysis process of the organic substances additives. The pyrolysis process, is the process by which a complete burn out of all organics out from the tape is achieved, without leaving any residues. Such residues would be detrimental to the sintering process of the tape, resulting in a porous, low density material for the generator.

The thermoelectric powder alloy produced in this project was found to have an average particle size of 3.15 μm, as

measured by the laser particle size analyser. An optimum average particle size was found through experimentation to be between 3–5 μm.

The third powder characteristic, is agglomerates. Agglomerates are one of the most important characteristics of powders, which must be identified and controlled.

The definition of agglomerates in a general sense, is a collection of particles bound together by surface forces and/or a solid bridge, to form free flowing units. The surface forces, may be electrostatic or Van der Waals attractions between particles or liquid capillary force due to the presence of liquid within the agglomerate [10].

It is the agglomerates which determine how a powder will flow or pack during handling. Much of the structure of the agglomerate is preserved in the green tape, which means that particle packing and porosity distribution in the tape are sensitive to the presence of powder agglomerates. Since the microstructure of the final product, developed during the sintering process, is dictated largely by the starting green tape microstructures, it is important to control the agglomeration problem within the green tape.

In the actual processing of the green tape in this project, an ultrasonic probe was used instead of the ball milling technique to break the powder agglomerates. The tip of the ultrasonic probe was immersed half way down in a mixture of solvent, powder and dispersant. Ultrasonic agitation was then carried out for 10 min, at No. 8 power setting, which gave a power input of 200 W. Since the sample is heated rapidly under this treatment, the polythene jar which contain the mixture was kept in a cold water bath at 15°C.

The time for sonification was decided after measuring the agglomerate's size against the sonfication time at maximum power, for a mechanically alloyed powder. Such powders normally represent the worst case of agglomeration, since many of its agglomerates are particles connected through weak solid necks as a result of cold mechanical welding. The agglomerate average size was measured by an optical microscope connected to a computer screen through a video camera. The size measurements were carried out through an image analysis software 'Lucia' from Nikon Ltd. The mixture consisting of powder and solvent was first mixed without any sonification, and a sample taken for analysis. The mixture was then subjected to sonification and a sample was taken every minute for analysis. Fig. 2 shows the reduction of the agglomerates size against time. The average agglomerate size for the unsonified mixture was 468 μm, which was reduced to 7 μm average size after 10 min of sonification. Thus, in comparison to the horizontal ball milling which requires at least a 48 h [11], the ultrasonic probe method was considered to be an effective, fast and cheap method for controlling agglomerates within a powder.

3.2. Slurry mixing

Conventionally most of the mixing in the tape casting process, is carried out by milling rather than mixing. The choice of the mixer over the ball mill in this project was influenced by the following reasons:

1. Most tape-casting processes, use milling to break down the agglomerates in the powder. However, the ultrasonic probe technique was employed in this project as a more effective and faster method.
2. It has been established by other researchers, that long milling times damages the binder molecules by the impact forces of the milling media resulting in degradation of the cast tape strength.
3. Milling procedures can introduced contamination to the slurry from the milling media and the mill linings.
4. The difficulties of draining the slurry out of the mill usually leads to some slurry wastage. Milling is usually carried with an excess amount of solvent to compensate for this, but this lengthens the de-airing process when removing the excess solvent from the slurry.

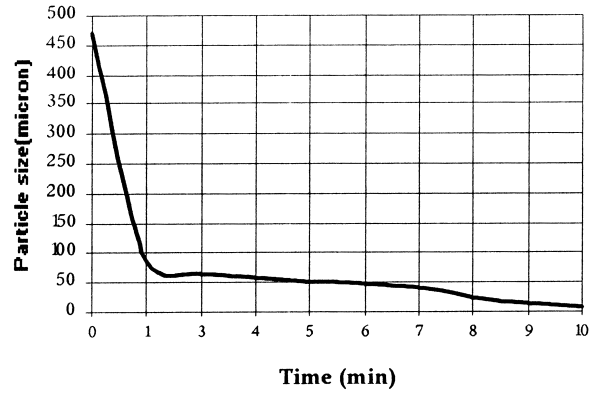

Fig. 2. Particle size vs. sonification time in minutes.

Before the mixing was started, a mixture of solvent, powder and dispersant were sonicated using an ultrasonic probe (Soniprobe automatic type 7532A, DAWE Inst. Ltd). Mixing was then started with organic additions being made at various times depending on the binder used.

It was found useful to add the binder to the mixture before the plasticizer. This is done to prevent the binder molecules from competing with the plasticizer molecules at the adsorption site on the powder particle surface [12].

3.3. Viscosity measurement

The process of tape casting is based on the interrelationships between slurry rheology and the green tape microstructure. Therefore, in order to improve the reliability of the characteristics of the green cast tape, the viscosity of the slurry must be well characterised before casting.

The viscosity of the slurry influences the following:

1. The rheological behaviour of the slurry with increasing shear rate and time.
2. The dispersion of the powder within the liquid and the presence of agglomeration.

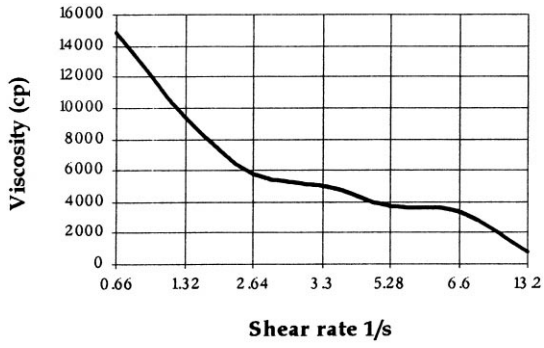

Fig. 3. Typical shear thinning behaviour of some slips used in this project.

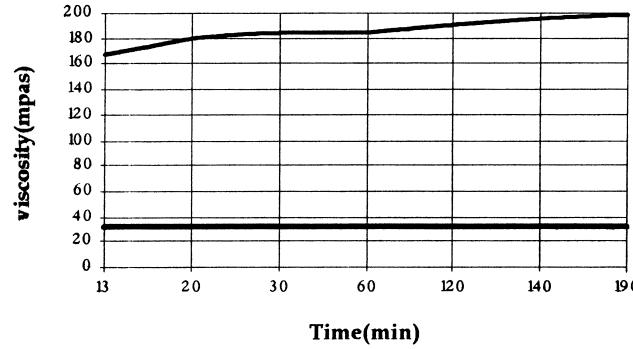

Fig. 5. A slurry viscosity measured at different shear rate.

3. The thickness of the green tape. The control of viscosity is achieved through controlling the amount of organics added to the mixture.

All slurries used in this work were found to be a shear thinning or a pseudo-plastic type. The shear thinning behaviour is caused by the alignment of binder molecules at high shear rate. This type of viscous behaviour was advantageous in the tape casting process [13]. This was because, the viscosity of such a slurry decreases with increase in the shear force, which occurs when the slurry passes under the casting blade. After passing the blade, no shear force was present and the viscosity of the slurry increased again. This action preserves the homogenous structure of the slurry by reducing the mobility of its constituents, requiring fast recovery to high viscosity. Fig. 3, shows a typical shear thinning behaviour for a slurry. Fig. 4 shows a typical viscosity against time graph measured at a low shear rate of 0.66 s^{-1}.

All the slurries used have showed rheopexic behaviour, increasing viscosity with time. Such behaviour is not expected, since these slurries resembled a thixotropic paint, or decreasing viscosity with time as shown . The reason for this might be due to flocculation. These flocs could be broken down at a high shear rate, and since most of the measurement have been conducted at a low shear rate, which might be insufficient to break them down in suspension. Indeed at a higher shear rate, only slight shear thickening and sometimes thixotropic behaviours have been observed, as shown in Fig. 5. Thixotropy is usually not a desirable feature when pesudoplastic behaviour is required. If the slurry remains at a low viscosity after being acted upon by the casting blade, the advantage of having a high viscosity at a low shear rate is not realised, a fast recovery to high viscosity when shear rate is reduced is essential.

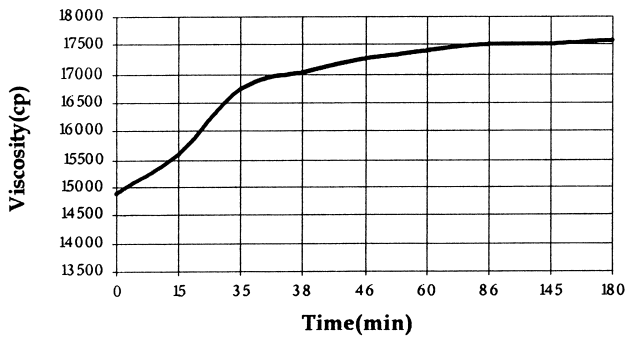

Fig. 4. Typical viscosity vs. time for a casting slurry measured at very low shear rate of 0.66 S^{-1}.

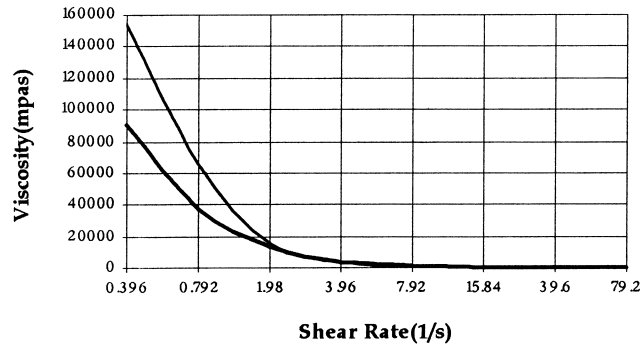

Fig. 6. Viscosities of sonified and unsonified slurries.

Fig. 6 shows the viscosities of two slurries, one mixed without any sonification and the second with 5 min sonification. The figure shows that the slurry which has been ultrasonically dispersed, has a much lower viscosity than the one which has had no treatment. As expected well dispersed particles flow more easily than if they were agglomerated. Large agglomerates tend to trap liquid within their pores, like a sponge, liquid that would otherwise act as a lubricant flow medium reducing the viscosity of the slurry.

Fig. 7 shows the way in which slurry viscosity varies with dispersant concentration. These measurement were made to optimise the dispersion of the powder within the slurry. This is shown by the lowest point on the viscosity curve. The optimum dispersion concentration is indicated by the minimum viscosity point.

Fig. 8 shows the effect of binder content on the viscosity of the slurry, for both PVB and PMMA binders. It can be seen, that the binders effect the slurry's viscosity in opposite ways. The PMMA decreases the slurry viscosity as its percentage increases, due to high dispersion of the powder particles and polymeric stabilisation mechanism. The PVB

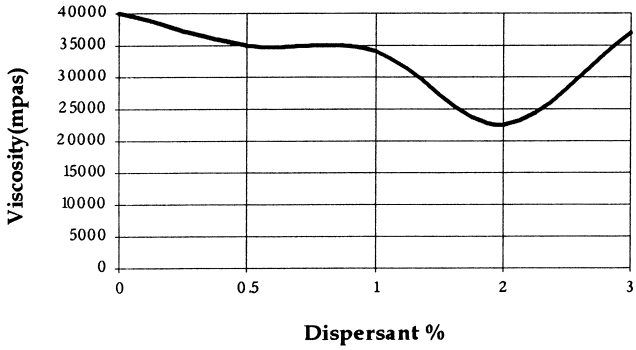

Fig. 7. Dependence of viscosity on dispersant concentration.

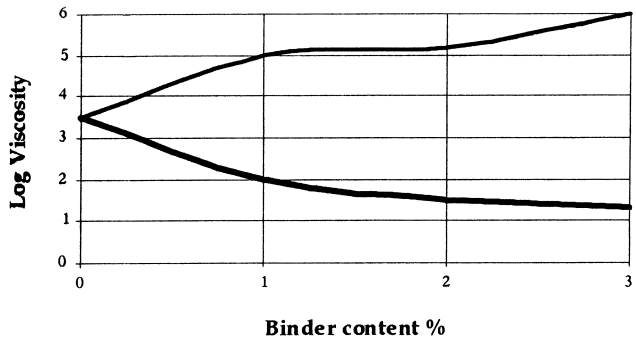

Fig. 8. Dependence of slurry viscosity on binder concentration for PVB and PMMA.

binder has lower dispersion power, resulting in increasing slurry viscosity with increasing binder content. This data is used when deciding the make up of a particular slurry.

3.4. The casting process of the green tape

After the mixing was complete, the de-airing process was carried out to eliminate air bubbles within the slurry and to remove excess solvent, thus controlling the slurry viscosity.

As shown in Fig. 1, a two blade configuration was used for precise thickness control of the cast tape. This configuration also minimised the hydrodynamic and surface forces as the slurry passed under the casting blades and this is achieved by adjusting the relative height of the two blades, to step the slurry thickness down progressively with each blade.

The pool height was kept to minimum by a slow flow of the slurry down the wall of the reservoir relative to the casting speed, in order to avoid turbulence and air bubbles in the slurry.

Other parameters that had some effect on the casting thickness were, the slurry viscosity dependent on solvents and the binder concentration and the casting speed. The casting speed had no real effect, provided the height of the casting pool was kept constant and low. In general, the casting speed was 30–40 cm min^{-1} for slurry viscosity in between 2000–10,000 MPas, while for higher viscosities the speed was not so critical.

Table 3
Side-flow factor for different casting blade heights and viscosities

Casting blade height (mm)	Viscosity (MPas) at shear rate 0.396 S^{-1}	S_F%
1–2	10000–50000	20
1–2	>50000	15
0.15–1	2000–10000	15
0.15–1	10000–50000	10

In order to estimate the thickness of the dry cast tape, an expression was developed accurate to within ±10%. The expression was based on three variables.

(i) The height of the second cast blade denoted by H_B.

(ii) The percentage of side flow to the original cast width of the tape denoted by S_F.

(iii) The volume fraction of solvent present within the slurry V_F.

The initial thickness of the wet cast tape H_B, was determined by the height of the second casting blade. The second variable S_F was determined by the viscosity of the slurry, the height of the casting blade and the surface tension between the slurry and the substrate. The S_F was determined empirically based on the casting blade height H_B and the slurry viscosity range, as shown in Table 3.

The third variable was the volume fraction of the solvent present within the wet tape. When drying is complete, the amount of shrinkage or reduction in thickness, is equivalent to the amount of solvent volume evaporated. It is important to mention, that a fraction of the solvent mixture estimated between 0.5 and 1%, always remains trapped within the organic matrix of the dry tapes, even after months from the time of casting [12]. To compensate for this effect, 1% of the solvent volume was subtracted. Therefore, the expression for estimating the thickness of the dry cast tape is equal to

$$\text{Thickness of cast tape} = H_B - (S_F + V_F)$$

Fig. 9 shows a graph of measured and calculated thickness for the dry cast tape for different heights of the casting blades.

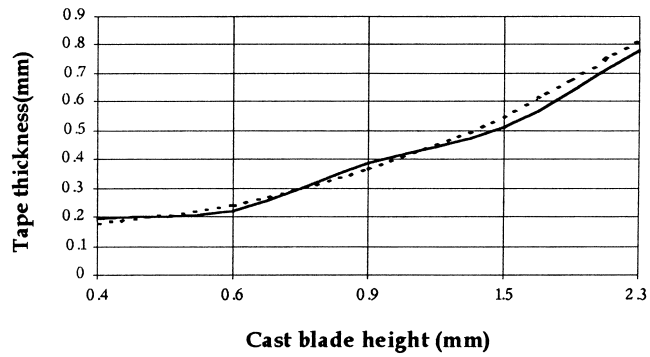

Fig. 9. Measured and calculated tape thickness as a function of cast blade height.

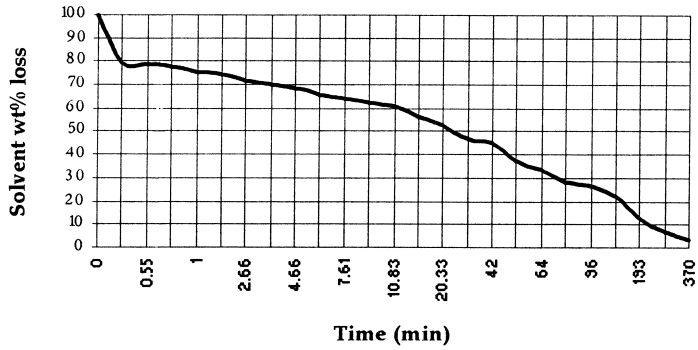

Fig. 10. Weight % loss of solvent mixture against time in minutes.

3.5. Drying, surface texture and cracks of cast tapes

The rate of drying and solvent evaporation, has been found to be a very important factor in determining the quality of the surface texture and the cracking induced in the cast tape during drying.

Fig. 10 shows the evaporation rate of an ethanol/trichloroethylene mixture from a cast tape in still air. It can be observed that the solvent evaporation is a two-stage process. In the first stage the tape is a liquid and the solvent flows through the tape by liquid diffusion or capillary action, and evaporates at the surface at a very fast rate. In the second stage the surface of the tape solidifies and the diffusion through that solid skin, is slow, which reduces the drying rate.

The surface texture of the tape, is defined by the amount of pores visible to the naked eye, and by the roughness of the surface.

The porosity and smoothness of the tapes were found to be largely dependent on the ratio of x and y and the solvent evaporation rate. Porous and rough tapes were usually obtained with a high x, low y and/or uneven evaporation of the solvent.

In general, the solvent evaporation must be slow, so that skinning and trapping of gas bubbles are avoided. Skinning reduces the rate of evaporation, and is represented in Fig. 10 by the slow second stage of evaporation. Skinning prevents the healing of the surface defects, like pores and prevents the migration of bubbles inside the tape to the surface. To prevent skinning from occurring the following steps were found to be very effective.

1. A two component solvent was used, with a highly soluble binder in ethanol, and low solubility binder in trichloroethylene. Since the ethanol evaporates at a faster rate than the trichloroethylene, the latter will precipitate in the binder matrix, which starts to form as the ethanol evaporates giving rise to some tape shrinkage. At the same time, the trichloroethylene remains as a residual liquid at the surface, and thus prevents a skin formation.
2. Drying the tape in still air or under a metal box cover was found to be detrimental to the surface texture of the tape, because of the formation of pools of solvent on the surface and as a consequence uneven shrinkage occurred. This problem was prevented by a slow airflow over the surface of the cast tape. The flow velocity should not be so fast as to cause skinning, an airflow rate of less than $0.4\ \mathrm{ms}^{-1}$ was found ideal for the ethanol/trichloroethylene mixture. The air temperature was kept at 50°C, well below the ignition point of 71°C of the solvent mixture. The direction of the air flow was opposite to the casting direction of the tape, hence the vertical gradients in the solvent concentration was reduced, guaranteeing a continuously drying rate in the tape.

The appearance of cracks in tapes was found to be very sensitive to the ratio of the solvent components. At a ratio below the azeotropic ratio of 2.78 for trichloroethylene/ethanol, all tapes developed cracks, regardless of the x and y ratios and the thickness of the tape. An azeotropic ratio is defined as the ratio of a solution at which the mixture has a uniform evaporation rate for both of its components, retaining its composition throughout the evaporation process.

Fig. 11, shows two regions of cracks and no cracks, with different parameters of x, y and the solvent ratio. The figure shows, that no cracks occur at and above a 2.78 solvent ratio, regardless of the changes which occur in the other parameters. This does not indicate that cracking is independent of the other parameters, but that they were not a significant factors in the crack formation.

3.6. Adhesion of cast tapes to substrate

The adhesion between the tape and the substrate or the tape carrier, must be small enough to allow for the dry tape to be peeled away from the substrate, but large enough to prevent curling of the tape, so that the shrinkage occurs in the thickness direction, perpendicular to the tape carrier, and not on the width of the tape.

The strength of the adhesion between the tape and substrate was found to be directly proportional to the ratio x and the surface tension of the substrate. Curling of the tapes on

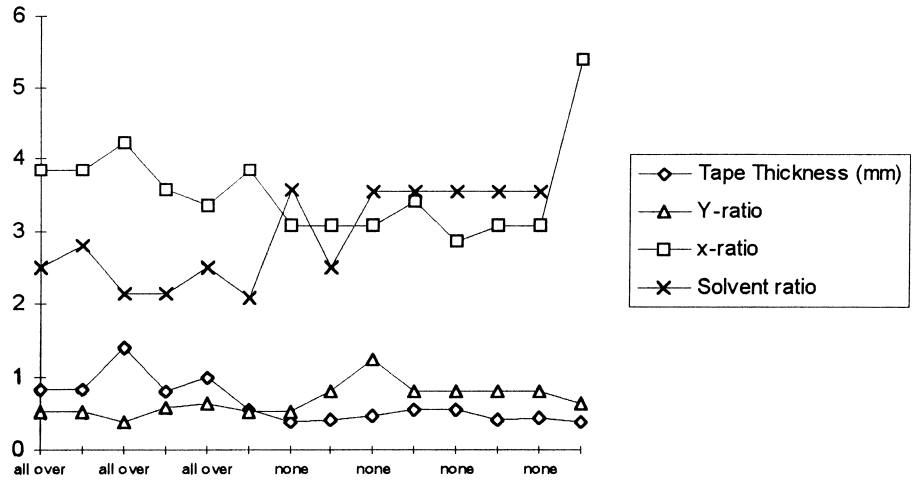

Fig. 11. Cracks in tapes against solvent, x, y ratios and tape thickness.

the other hand was found to be directly proportional to the y ratio.

The organic additives in the tape, and especially the binder, have a higher surface tension than the inorganic powder. Hence as the ratio x increases, or as the binder content decreases, the adhesion to the substrate increases.

As y increases, two conditions starts to arise which increase the probability of tape curling during drying. Increasing y, implies increasing the binder content, and hence shrinkage occurs in all directions, including the sides of the tape. Also increasing y, can imply decreasing the amount of plasticizer which distributes the binder uniformly in the tape, and can therefore lead to an uneven binder distribution with uneven shrinkage, possibly leading to curling.

Some guidelines have been established to minimise tape adhesion to the substrate

1. The difference between the surface tension of the tape and the substrate should be as large as possible, where the former should posses the largest value of the two. This gives a low contact angle between the two surfaces, a low wetability, and a poor adhesion joint. This is achieved by using a low x ratio.
2. High slurry viscosity, minimises the slurry spread over the substrate and reduces adhesion.
3. The surface of the substrate should posses some minimal roughness, which will not effect the overall surface smoothness of the tape, but allows the creation of some defects, between the two surfaces, and induces a higher friction coefficient to minimise spread. This surface roughness perhaps contributes to the better performance of the polythene surface over the smooth surfaces of the glass and the PTFE substrates.

When the tape is dried, the force required to remove it from the substrate without causing any damage, had to be less than the tensile strength of the tape. The removal force was found to be dependent upon two conditions. The pulling angle θ that the tape makes with the substrate during removal, which had to be as low as possible and the drying time which had to be long enough for the tape to develop some tensile strength but not so long as to form a strong adhesion to the substrate.

3.7. Tensile strength of cast tape

The measurement of the tensile strength of the cast tape was carried out on specimens, cut from each tape. The test specimen was 60 mm long, with a neck of 30 mm in length and 10 mm in width. These specimens were hung on a spring balance, and weights were added gradually until the tape fractured.

The tensile strength increased with the increase of organics in the tapes or a decrease in the x ratio. The tensile strength was found to increase as the amount of binder in the tape was increased. Fig. 12, shows this relationship, where all the constituents are kept constant as the binder content was varied.

Increasing the amount of binder in the tape, increases the tensile strength, but also increases the rigidity of the tape. A balance between rigidity and flexibility was required for

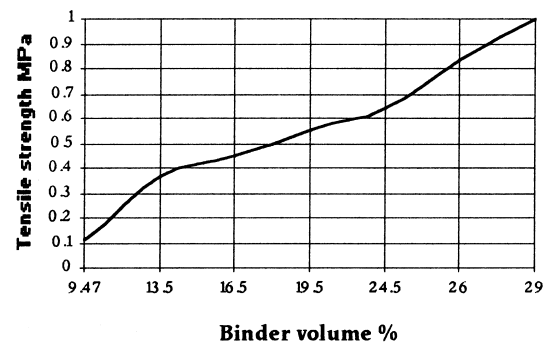

Fig. 12. Maximum tensile strength (MPa) of tape as a function of binder content.

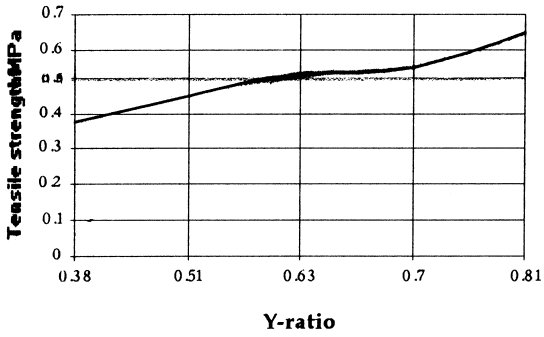

Fig. 13. Maximum tensile strength (MPa) of tape as a function of ratio *y*.

shaping, adhesion and the lamination processes. This balance was achieved by varying the ratio *y*, as shown in Fig. 13. The best tape to satisfy the requirements in term of handling and lamination was found to have a *y* ratio of 0.81.

3.8. Lamination of green tapes

Lamination or pressing of green tapes, is usually carried out to build up the thickness of a single material tape or to obtain a monolithic layer consisting of different materials.

The green tapes were first stacked on the top of each other in a stainless steel mould. The mould was then heated up to 60–65°C before an axial pressure, of between 20–200 MPa, was applied to the tapes for 3 min. The purpose of the heat, was to soften the organic materials (i.e. binders and plasticizers) to a point where the pressure applied would be easily transferable through the stacked layers, helping to diffuse the layers one into another. The tapes were considered laminated, when they could not be stripped from each other without tearing. As the ratio *x* in the tapes was increased, more pressure was needed to achieve lamination. Fig. 14, shows the pressure which had to be applied to the tape stack to produce lamination.

From Fig. 14, it was observed that the pressure needed to achieve lamination is drastically increased as the value of *x* increased above 62%. Since one of the objectives of this project was to use as little organics as possible, and yet still produce a tape which respond subsequently to all processing following casting. The effect of the ratio *y* was studied for an *x* value of 64%, while keeping the applied pressure fixed at 100 MPa. Delamination was observed to occur for *y* values of less than 0.81 for the poly-vinyl-butyral binder, and for a *y* value of less than 2.5 for the PMMA binders. The reason for the delamination was believed to be due to the plasticizer which acts as a lubricant between the layers, thus preventing adhesion between the tapes. Hence more pressure is needed to achieve lamination as the *y* value is decreased.

3.9. Bulk and apparent density of tapes

The measured densities of the green tapes gives only an insight into the amount of open porosity present within the green tape. If the packing of the thermoelectric powder material is required to be assessed, then the densities of the organic additives within the tapes, must be accounted for and subtracted from the measured density.

A comparison of bulk and apparent densities of measured green tapes is shown in Fig. 15 as a function of the organic additives percentage in the tape. From the figure, it can be seen that the values of the bulk and the apparent densities converge as the organic content increases, or the value of the *x* ratio decreases.

Since the difference between the bulk and the apparent densities represents the amount of open porosity within the tape, the increase in the bulk density value towards that of the apparent density, represent the filling of the open pores with organic materials.

Fig. 15 is important, because the meeting point of the bulk and the apparent densities curves, represent the maximum allowable quantity of organic additives, that can be used in the formulation of the tape, and the tape is free from open pores. In practice, excessive amounts of organic additives are detrimental to the tape during the pyrolysis process, with a lower content of organic additives, a balance is achieved between good quality tape suitable for handling, at the same time having an efficient and easy organic burn out during the pyrolysis.

The effect of the binder to plastizer content (*y* ratio) on the bulk and the apparent densities of the green tape was

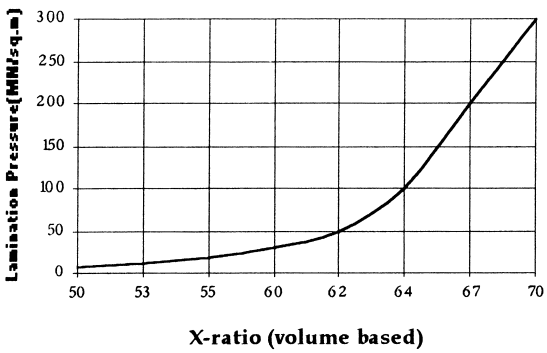

Fig. 14. Lamination pressure (MPa) as a function of the *x*-ratio (heat and pressure).

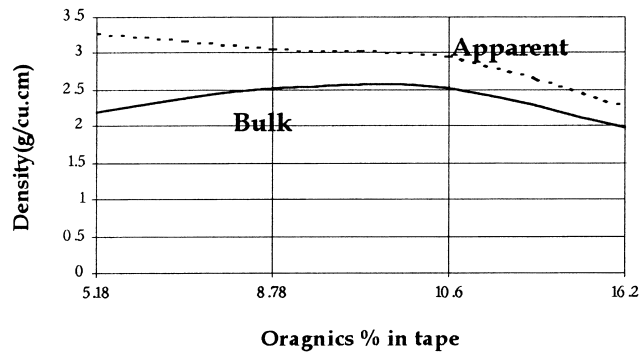

Fig. 15. Bulk and apparent densities as a function of the organic content of the tape.

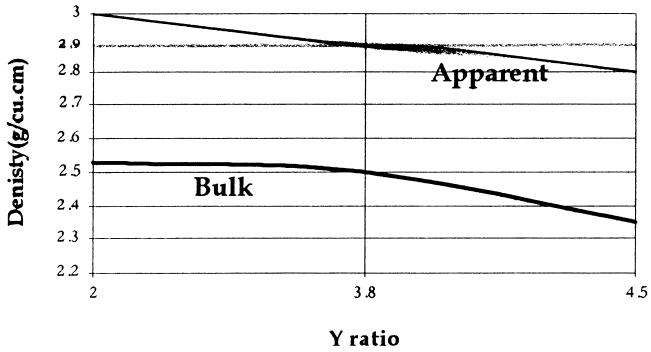

Fig. 16. Bulk and apparent densities of green tapes as a function of the *y*-ratio.

investigated by keeping the ratio *x* constant, while varying the *y* ratio. Fig. 16 shows a graph of bulk and apparent densities as a function of *y*.

From Fig. 16, it was observed that as the *y* ratio increased, lower bulk and apparent density was obtained. This was believed to be due to the uneven distribution of the binder in the tape, which occurred with a low *y* ratio, leading to increased porosity within the tape.

4. Conclusions

Two types of slurry formulation based on Poly-vinyl-butyral (PVB) and Poly-methyl-methacrylate (PMMA) binders were used to produce green tapes made out of thermoelectric material powders. Powder agglomerates in the slurry were controlled by the use of ultrasonic vibration. Laser particle size analysis and SEM were used to determine an optimum vibration time of 10 min to reduce and breakdown most of the agglomeration within the slurry. The effect of the organic additives on the green tape physical characteristics were assessed, in term of the ratio of the inorganic to the total present in tape *x*, and the ratio of binder to plasticizer *y*. The cast green tape were characterised by powder particle size, slurry viscosity, apparent and bulk densities, tensile strength, adhesion properties of tape to substrate and the necessary pressure of lamination to produce a monolithic multi-layer made out of different materials.

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